

Minor Elements in Nakhlite Pyroxenes: Does Cr record changes in REDOX conditions during crystallization? G. McKay¹, C. Schwandt², L. Le², and T. Mikouchi³, ¹Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, ²ESC Group, NASA Johnson Space Center, ³Dept. of Earth and Planetary Science, Univ. of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan.

Introduction: Nakhrites are olivine-bearing clinopyroxene cumulates [e.g., 1]. Based on petrographic characteristics, they may be divided into groups that cooled at different rates and may have been formed at different depths in a single flow [e.g., 2, 3]. The order of cooling rate from slowest to fastest is NWA998 < Lafayette < Governador Valadares ~ Nakhla < Yamato000593 < NWA817 ~ MIL03346. Nakhlite cumulus pyroxene grains consist of large cores that are nearly homogeneous in major element composition surrounded by thin rims that are zoned to Fe-rich compositions. Detailed study of these pyroxenes is important because they retain a record of the crystallization history of the nakhlite magma. Moreover, because the composition of the nakhlite parent melt cannot be directly determined, “inversion” of the major and minor element composition of the cumulate pyroxene cores can be used to estimate the composition of that melt. Moreover, minor and trace element zoning of pyroxenes can provide information about the oxidation conditions under which these samples crystallized [e.g., 7]. Thus it is important to understand the major and minor element zoning in the cumulus pyroxenes. While major elements are nearly homogeneous, minor elements exhibit distinctive zoning patterns that vary from one nakhlite to another [e.g., 3,4]. This abstract reports unusual Cr zoning patterns in pyroxenes from MIL03346 (MIL) and contrast these with pyroxenes from Y593 and Nakhla.

Minor Element Zoning: Nakhlite pyroxenes are zoned in Al, Ti, and Cr. Al and Ti are strongly correlated, but Cr is not correlated with these elements. Pyroxenes from slowly cooled nakhrites generally exhibit a bimodal zoning pattern for Al and Ti, but rapidly-cooled sample MIL has a single mode of Al concentrations (Fig. 1-2) [3]. The origin of this zoning is not completely understood. However, by analogy with pyroxenes from our experimental runs, we believe that it is likely produced by sector zoning during growth.

Cr is depleted in the outer Fe-rich *rim*s of all nakhlite pyroxenes as a result of normal fractional crystallization. On the other hand, Cr exhibits only minor zoning in the homogeneous *cores* of slowly cooled nakhrites, but is complexly zoned in rapidly cooled MIL pyroxenes (Fig. . In MIL, Cr is depleted in the central portions of the “homogeneous” pyroxene grains, and enriched in the outer portions of the cores. Moreover, Cr zoning in MIL cores has a bimodal distribution (Fig 3-4) and is not correlated with Al zoning. In contrast, Nakhilite pyroxenes lack the low-Cr “hump” seen in MIL pyroxenes (Fig 5).

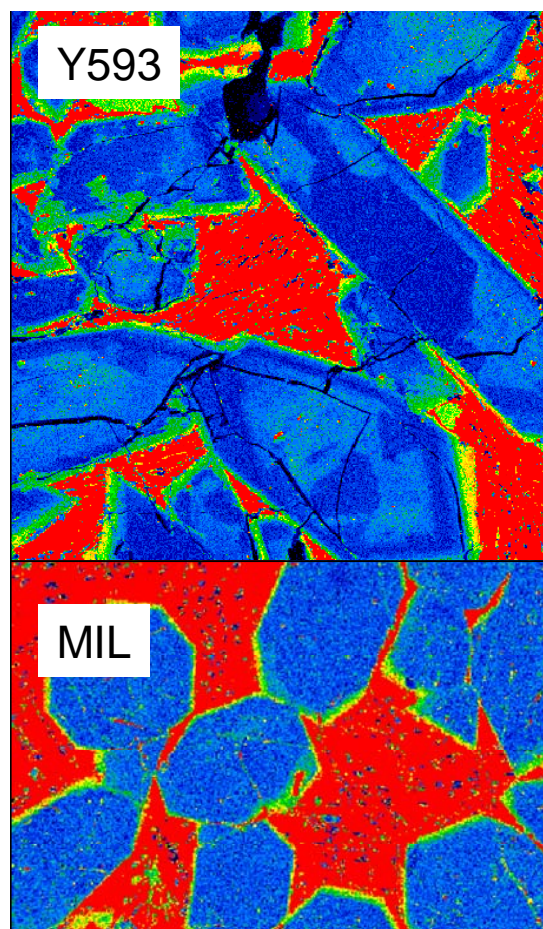


Fig. 1. Al maps of Y593 and MIL. Field of view is about 2 mm. Note patchy zoning in Y593, typical of zoning in slowly cooled nakhrites, and lack of zoning in MIL.

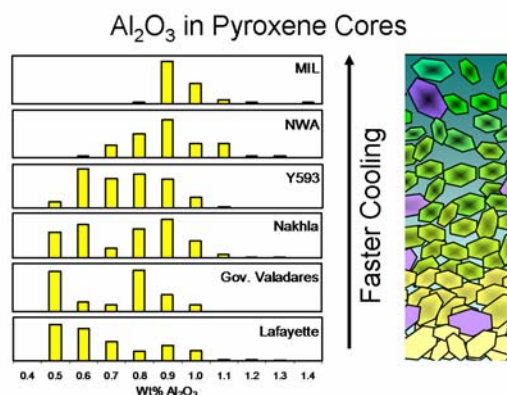


Fig. 2. Histograms of Al content in nakhlite pyroxenes, arranged according to estimated cooling rates [2].

Except for the outer Fe-enriched rims, the MIL zoning pattern is in marked contrast to that expected during normal fractional crystallization.

Discussion. The source of the unusual Cr zoning in MIL is difficult to understand. Fractional crystallization would be expected to produce the opposite pattern, i.e. Cr depletion from core to rim. Is it possible that the Cr zoning might reflect a change in oxidation state of the magma during crystallization of the pyroxenes? At constant Al, average $D(\text{Cr}, \text{Px}/\text{L})$ in our nakhilite experiments increases by nearly a factor of 2 as oxygen fugacity increases from IW to QFM (Fig. 6). This probably reflects the ease of charge balancing in the presence of increased amounts of Fe^{+3} . MIL has been reported to have large amounts of trivalent Fe compared with other nakhilites [5,6]. However, stoichiometry from high-precision electron microprobe traverses across MIL pyroxenes indicate that, if anything, the Cr-poor portions are *more* oxidized than the Cr-poor cores. In particular, differences in cation sums between Cr-poor and Cr-rich MIL pyroxenes can be reconciled if ~1% more of the Fe in the Cr-poor regions is trivalent relative to Fe in the Cr-rich regions. However, this observation is inconsistent with the idea that higher Cr contents in the outer parts of the pyroxene rims result from enhanced Cr partitioning due to oxidation during crystallization. This result awaits validation by more sensitive techniques such as V oxybarometry [7], but for now there is no evidence supporting a progressive oxidation during crystallization of the homogeneous core pyroxenes in MIL. This conclusion is consistent

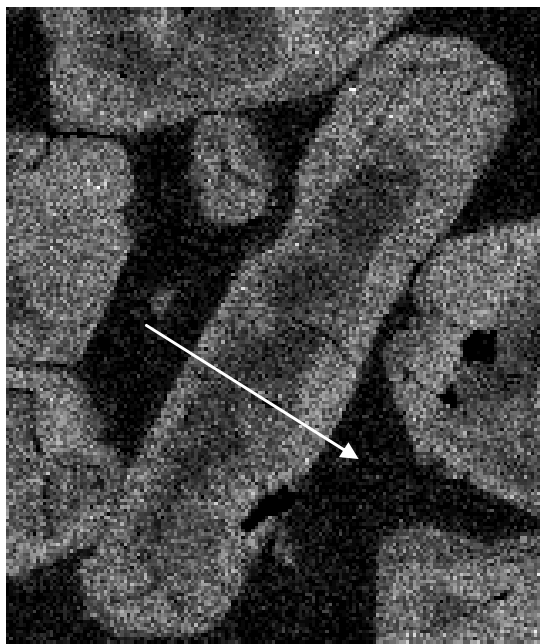


Fig. 3. Cr map of MIL pyroxenes. Note Cr depletion in center of grains relative to margin. Cr-enriched portion is outer part of core that is homogeneous with respect to major elements. Arrow shows location of microprobe profile in Fig. 4.

with results presented in a companion abstract [8].

References: [1] Wadhwa (2001) *Science* 291, 1527. [2] Mikouchi *et al.* (2006) *LPSC* 37, #1865. [3] McKay *et al.* (2005), *MAPS* 40, 5335. [4] McKay *et al.* (2006) *LPSC* 37, #2435. [5] Morris *et al.* (2006) *LPSC* 37, 1594. [6] Dyar M.D. *et al.* (2005) *JGR*, 110, doi:10.1029/2005JE002426. [7] Karner *et al.* (2007), *LPSC* 38. [8] Makishima *et al.* (2007) *LPSC* 38.

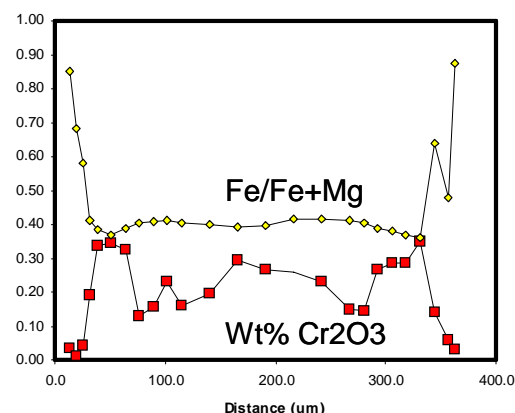


Fig. 4. Microprobe profiles across MIL pyroxene in Fig. 3. Note that Cr enrichment is within homogeneous core (constant Fe/Fe+Mg).

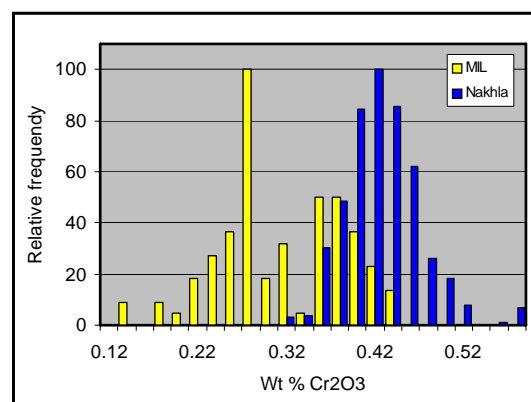


Fig 5. Comparison of Cr content of pyroxene cores from slowly cooled Nakhla and rapidly cooled MIL.

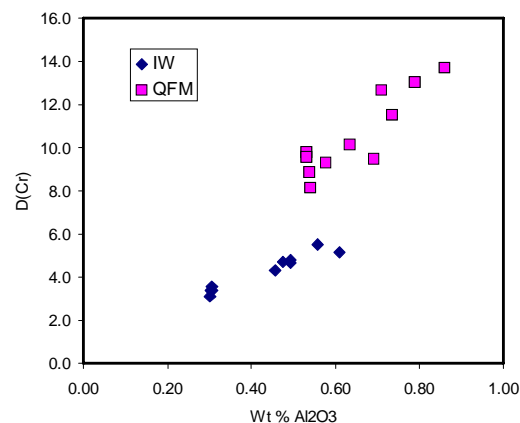


Fig. 6. Pyroxene/melt partition coefficients from nakhilite crystallization experiments. Note that at constant Al, D values increase ~2x as oxygen fugacity increases from IW to QFM.